Highly selective catalytic propylene glycol synthesis from alkyl lactate over copper on silica: Performance and mechanism

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ABSTRACT

Catalytic alkyl lactate hydrogenolysis over silica-supported copper at atmospheric hydrogen pressure and temperature range 433–493 K provides an eco-friendly green alternative to the petroleum-based process for propylene glycol synthesis. It was shown that catalytic activity strongly depends on copper loading and the most active catalyst contains ca. 45 wt.% Cu. General peculiarities of methyl and butyl lactate hydrogenolysis were studied demonstrating that an overall reaction rate increases with reaction temperature increase but a selectivity to propylene glycol decreases due to enhanced concurrent dehydrogenation of propylene glycol to a by-product hydroxyacetone. It was found that the amount of propylene glycol formed during the reaction is determined by thermodynamic equilibrium between propylene glycol and hydroxyacetone that results in propylene glycol selectivity of 96% at full butyl lactate conversion at 453 K. Overall mechanism of alkyl lactate transformation involving formation of intermediate hemiacetal over bifunctional Cu/SiO_2 catalyst was proposed.

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1. Introduction

Currently, the attention of the world scientific community is increasingly focused on environmental protection and efficient use of natural resources as well as on energy saving. A huge number of scientific publications on biomass transformation into valuable commercial chemicals have appeared recently [1,2]. At the same time, the efficient use of secondary products of biomass processing is vitally important, because it is aimed not only at the development of new environmentally benign technology, but also simultaneously solves the problem of industrial and agricultural waste utilization. Moreover the molecules extracted from renewable sources already contain functional groups and, therefore, number of steps for the synthesis of chemicals from the biomass components is less than from fossil fuel [3–5]. Nowadays design of the new catalytic routes starting from platform molecules derived from renewables and different from the traditional chemical synthesis routes starting from fossil fuels is one of the key issues of sustainable development [6]. Thus, commercial production of propylene glycol widely used as a solvent or a reagent in pharmaceutical and chemical industries is currently petroleum-based and involves high pressure and high temperature hydrolysis of propylene oxide produced by either chlorohydrin process or the

per-oxidation process which is unfavorable from green chemistry viewpoint. A catalytic method starting from lactic acid obtained by fermentation of crude biomass provides an eco-friendly alternative to the petroleum-based process for 1,2-propanediol synthesis. Moreover this method is carbon efficient, since implies hydrogenation of −COOH moiety to −COH without any loss of carbon atoms. However it is well known that catalytic hydrogenation of carboxylic acid to corresponding alcohols is a very difficult process, which requires high pressure and temperature [7]. For example, hydrogenation of lactic acid to propylene glycol over Ru-containing catalyst was carried out at 14.5 MPa and 423 K leading to noticeable lactic acid conversion and selectivity to propylene glycol [8]. Silica-supported copper prepared by incipient wetness impregnation was proven to be a highly selective catalyst to convert lactic acid to 1.2-propanediol at low hydrogen pressure [9]. Lactic acid hydrogenation in vapor-phase over 10 wt.% Cu/SiO_2 catalyst leads to 7.3% conversion and 75% selectivity to propylene glycol at 1 bar hydrogen pressure. However, several drawbacks have arisen during direct hydrogenation of lactic acid such as catalyst deactivation due to polymerization of lactic acid and formation of undesirable propionic acid. Apparent disadvantage of this process is low productivity to the desired propylene glycol.

To perform the hydrogenation process more effectively carboxylic acids are usually converted into more readily reducible esters [10]. Hydrogenolysis of alkoxy group in liquid phase was first reported under high hydrogen pressure over copper chromite as one of the most effective and widely used catalysts for

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ester hydrogenolysis [11,12]. For example Adkins and co-workers achieved 80% yields of propylene glycol from methyl lactate over copper/chromium oxide and Ni Raney catalysts at temperature 423–523 K and hydrogen pressures 20–30 MPa. Copper chromite also shows significant activity in butyl lactate hydrogenolysis only at elevated hydrogen pressure in autoclave at 15–20 MPa and 498 K resulting in the conversion of butyl lactate of 91% and selectivity to propylene glycol of 89% after 2 h [13]. Luo and co-workers achieved 91.5% conversion of ethyl lactate and 90.7% selectivity to propylene glycol in autoclave at 5.5 MPa and 423 K over Ru–Sn/γ-Al$_2$O$_3$ after 10 h [14,15].

The serious disadvantage of all mentioned liquid phase processes is a necessity to use high hydrogen pressure and/or utilization of an expensive noble metal. In addition high catalyst loading is necessary to get relatively high yields. Carrying out hydrogenation in a vapor phase allows lowering hydrogen pressure. For example hydrogenation of organic esters to alcohols and glycols in a vapor phase over copper-zinc oxide catalysts was carried out at 507 K under 1.6 MPa (liquid hourly space velocity (LHSV) of 1.06 h^{-1}) giving 34.7% conversion of ethyl lactate and 97.7% selectivity to propylene glycol [16]. Despite these efforts a need for further search of an active catalyst and investigation of the effect of various reaction parameters on catalyst stability and selectivity to propylene glycol remains challenging.

A lot of debates were hold concerning mechanism of ester hydrogenolysis. Although hydrogenolysis of esters with a simple structure such as ethyl acetate and ethyl formate was studied rather intensively, until now there is no generally accepted opinion on the mechanism of this reaction which can proceed either with intermediate hemiacetal formation [17] or via dissociative adsorption of ester [18]. During a study of methyl acetate hydrogenolysis by a method of labeled atoms it was detected that an alkoxy fragment is quickly converted to alcohol while an acyl group exists on a copper surface for a long time [19,20]. Hence, the rate determining step is hydrogenation of acyl fragment adsorbed on copper surface. These acyl species can either be converted into alcohol, or desorbed to form aldehyde which is then converted into alcohol [17,21]. It has been also shown that the rate of acetaldehyde transformation is three orders (6000 times) higher than that for ethyl acetate [22]. It was suggested that the amount of aldehyde in the reaction products is defined by thermodynamic equilibrium between alcohol and aldehyde. While alkyl formate hydrogenolysis proceeds, apparently, without dissociation of C—O bond in the initial ester [23], the mechanism for more complicated esters such as lactates is still not clear.

As a continuation of earlier investigation [24,25] we were focusing on feasibility of propylene glycol synthesis via copper catalyzed hydrogenolysis of methyl and butyl lactates under mild reaction conditions, where respectively methanol or butanol, released in hydrogenolysis can be recycled back to preceding esterification step. The goal of the present work is to study an effect of copper loading, an impact of alkyl substitute length and an influence of reaction conditions such as temperature, space velocity, and solvent nature in order to develop highly selective green catalytic process of propylene glycol synthesis under mild reaction condition.

2. Experimental

2.1. Catalyst preparation

Catalyst precursors were prepared by a homogenous deposition–precipitation method using decomposition of urea at 363 K. Aerosil 300 silica suspension in water and appropriate amounts of copper nitrate trihydrate (Saksk, Russia, >99% pure) together with urea (Cherkassk, Ukraine, >99% pure) were heated to 363 K and kept at this temperature for 20 h. After cooling the precipitate was filtered, washed and dried at 393 K. Calcination in air was carried out at 723 K [26]. Detailed description of catalyst preparation and characterization by DTA, DTG and XRD was published earlier [25,27].

2.2. Copper surface determination

The copper surface area was determined by a modified method described by Evans et al. [28]. The method was based on the decomposition of a nitrous oxide molecule on a copper surface followed by appearance of dinitrogen. A weighed sample of the oxide catalyst precursor was placed into a temperature-controlled fixed-bed reactor and reduced in a hydrogen flow at 653 K. After the catalyst was reduced, the reactor was cooled in a hydrogen flow to 333 K. Then exactly measured portions of nitrous oxide in a helium flow were injected by pulses into the reactor. Quantitative analysis of gas mixtures at the outlet of the reactor was carried out by GLC on an LKhM-80 chromatograph (NPO Agropribor, Russia) using a heat-conductivity detector and helium as a carrier gas. The components were separated on a Porapack Q capillary column (71 m × 0.5 mm × 0.05 mm). Injection of nitrous oxide pulses was stopped when nitrogen formation was not observed longer. The specific surface was calculated as follows. The surface area occupied by a surface copper atom located at the faces (1 0 0), (1 1 0), and (1 1 1) is 0.065, 0.092 and 0.0563 nm^2, respectively. If the copper surface is presented by these faces in an equal ratio the average surface area occupied by one copper atom is 0.0711 nm^2. According to the stoichiometry of the reaction, the formation of one nitrogen molecule is accompanied by the oxidation of two copper atoms. Then the metal surface can be determined by the following equation

$$S(\text{Cu}) = 14.2 \times 10^{-20} \cdot v(\text{N}_2) \cdot N_A,$$

where $v(\text{N}_2)$ is the number of moles of nitrogen, and N_A is Avohadro's number.

2.3. Catalytic experiments

The experiments on hydrogenolysis of lactic acid esters were carried out in a vertical U-shaped flow reactor under hydrogen flow (10 L h^{-1}) at atmospheric pressure in a temperature range of 433–493 K. The hydrogenolysis unit was composed of a feeding system, a reactor, and a condensation system, as shown in Fig. 1. The reactor represents a quartz tube (internal diameter of 10 mm, length of 100 mm, and thickness of 1 mm) equipped with a thermocouple and heated by a furnace. In hydrogenolysis experiments, neat methyl or butyl lactates were fed into the reactor using a syringe pump, vaporized in the preheated line and mixed with purified hydrogen, thereafter the vapor mixture passed through the catalyst bed. In some hydrogenolysis experiments methyl lactate was diluted by water or methanol. The volatile products were collected in a downstream trap with liquid nitrogen.

The reactor was loaded prior to the experiments with catalyst grains (0.5 g, 0.25–0.5 mm) diluted by inert quartz beads (3 g, 0.63–1.6 mm) to provide proper length of catalyst bed and to avoid overheating of catalyst particles during hydrogenolysis. Reductive activation of copper hydroxysilicate precursors was performed in hydrogen flow at 523–653 K for 2 h in the same reactor prior to hydrogenolysis of alkyl lactate. Reductive activation temperature of Cu/SiO$_2$ was selected on the basis of preliminary catalyst investigation by TPR H$_2$ [27].
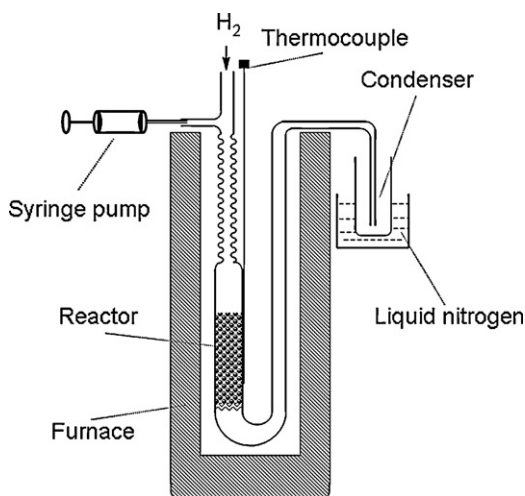
Fig. 1. A schematic picture of the hydrogenolysis reactor.

2.4. Products analysis

^{1}H NMR spectra were recorded on Bruker WPX-250 250 MHz instrument in CDCl$_3$ at room temperature. Chemical shifts are given in ppm from TMS using CHCl$_3$ as an internal standard (δ = 7.24 ppm). GC/MS analysis of butyl lactate hydrogenolysis products was performed with Agilent 5973N EI/PCI instrument equipped with a HP-5ms column (30 mm × 0.25 mm). Condensable products were quantitatively analyzed by a gas–liquid chromatography method (FID) using Chromosorb 101/5% FFAP packed glass column (2 m × 2 mm).

3. Results and discussion

Methyl and butyl lactate hydrogenolysis experiments were carried out in a kinetic regime when influence of mass transfer limitations was negligible. More details will be presented in Section 3.6.

3.1. Product analysis and identification

According to GC/MS, the main products of neat methyl and butyl lactate hydrogenolysis were propylene glycol, hydroxyacetone and a corresponding alcohol–methanol or butanol. 1-Propanol and 2-propanol were also detected in the reaction mixture in total amount about 2 wt.%. Methyl formate and dimethyl ether were also detected in the products mixture during methyl lactate hydrogenolysis. The ^{1}H NMR results clearly show the absence of 2-hydroxypropanal in the products mixture which indicates its fast further conversion under explored reaction conditions (*cf* [9], see Supplementary data, Figs. A1 and A2 for ^{1}H NMR spectra; Figs. A3–A9 for GC/MS).

Chemical shifts assignments for reaction products in butyl lactate hydrogenolysis are shown in Table 1, being in line with the literature. Reaction mixture of butyl lactate hydrogenolysis, ^{1}H NMR (250 MHz, CDCl$_3$) δ 0.78 (t, *J* = 5.6), 0.80 (t, *J* = 7.5), 0.98 (d, *J* = 6.3), 1.05 (d, *J* = 6.0), 1.18–1.32 (m), 1.27 (d, *J* = 6.6), 1.30–1.45 (m), 1.45–1.57 (m), 2.03 (s), 2.04 (s), 3.33 (ABX, *J* = 11.3, 11.0, 7.5), 3.46 (t, *J* = 6.6), 3.73 (m.), 3.86 (sept, *J* = 6.0), 3.95–4.09 (m), 4.12 (s), 4.14 (q, *J* = 6.6).

Chemical shifts assignments for propylene glycol dehydrogenation products are shown in Table 2 confirming identification of reactants. Reaction mixture of propylene glycol dehydrogenation, ^{1}H NMR (250 MHz, CDCl$_3$) δ 0.98 (d, *J* = 6.3), 1.05 (d, *J* = 6.0), 2.03 (s), 3.33 (ABX, *J* = 11.3, 11.0, 7.5), 3.73 (m), 3.86 (sept, *J* = 6.0), 4.12 (s).

Table 1
Chemical shifts assignments for butyl lactate hydrogenolysis products. Corresponding protons are designated with bold type.

Chemical shift (ppm)	Multiplicity	Protons designation
0.78	Triplet	**CH$_3$**CH$_2$CH$_2$CH$_2$OH
0.80	Triplet	CH$_3$CH(OH)COOCH$_2$CH$_2$CH$_2$**CH$_3$**
0.98	Doublet	**CH$_3$**CH(OH)CH$_2$OH
1.05	Doublet	(**CH$_3$**)$_2$CHOH
1.18–1.32	Multiplet	**CH$_3$**CH(OH)COOCH$_2$CH$_2$CH$_2$CH$_3$
1.27	Doublet	CH$_3$**CH$_2$**CH$_2$CH$_2$OH
1.30–1.45	Multiplet	CH$_3$CH$_2$**CH$_2$**CH$_2$OH
1.45–1.57	Multiplet	CH$_3$CH(OH)COOCH$_2$**CH$_2$**CH$_2$CH$_3$
2.03	Singlet	**CH$_3$**C(O)CH$_2$OH
2.04	Singlet	CH$_3$C(O)CH$_3$
3.33	ABX pattern	CH$_3$CH(OH)**CH$_2$**OH
3.46	Triplet	CH$_3$CH$_2$CH$_2$**CH$_2$**OH
3.73	Multiplet	CH$_3$**CH**(OH)CH$_2$OH
3.86	Septet	(CH$_3$)$_2$**CH**OH
3.95–4.09	Multiplet	CH$_3$CH(OH)COO**CH$_2$**CH$_2$CH$_2$CH$_3$
4.12	Singlet	CH$_3$C(O)**CH$_2$**OH
4.14	Quartet	CH$_3$**CH**(OH)COOCH$_2$CH$_2$CH$_2$CH$_3$

3.2. Effect of copper loading

It was found that copper hydroxysilicate exhibits catalytic activity in hydrogenolysis only after reduction in hydrogen atmosphere. Thus it seems to be reasonable to relate its catalytic activity to the metallic copper formed after reduction. "Chrysocolla" phase of copper catalysts was shown to play a key role in catalytic lactic acid hydrogenation [24]. To estimate the influence of copper loading on activity of silica-supported copper catalysts in lactate hydrogenolysis the copper loading was varied from 14.2 wt.% to 45.5 wt.%. The latter value was chosen because above 45% loading bulk copper oxide particles are formed on the catalyst surface along with chrysocolla phase. After reduction in hydrogen these copper oxide particles lead to lower dispersion of metallic copper. This maximum copper content was divided by 2 or 3 giving copper loadings of 22 wt.% and 14.2 wt.% respectively. More details about "chrysocolla-like" copper catalysts are reported in [25].

Metallic copper specific surface area of 14.2 wt.% and 45.5 wt.% Cu/SiO$_2$ catalysts was determined by nitrous oxide titration to be 12 m^2/g and 11 m^2/g respectively. Although metallic copper specific surface areas of 14.2 wt.% and 45.5 wt.% Cu/SiO$_2$ catalysts have close values, conversion of methyl lactate increases with increasing copper content, with the most active catalyst being 45.5 wt.% Cu (Fig. 2a). Selectivity to propylene glycol slightly decreases with increase of temperature and seems to be independent on copper content (Fig. 2b). Note that the crystal structure of the most active 45.5 wt.% Cu/SiO$_2$ catalyst precursor is very similar to mineral chrysocolla with an insignificant excess of silicon dioxide [27]. Copper ions in chrysocolla are reduced at temperatures above 458 K, and reduction of the sample at 543 K leads to formation of highly dispersed metallic copper particles of the size 3–8 nm distributed on SiO$_2$ surface [29]. To evaluate an intrinsic activity the catalytic activity is expressed in terms of TOF based on Cu surface area values. It was found that TOF increases with copper loading (Fig. 3).

Table 2
Chemical shifts assignments for propylene glycol dehydrogenation products. Corresponding protons are designated with bold type.

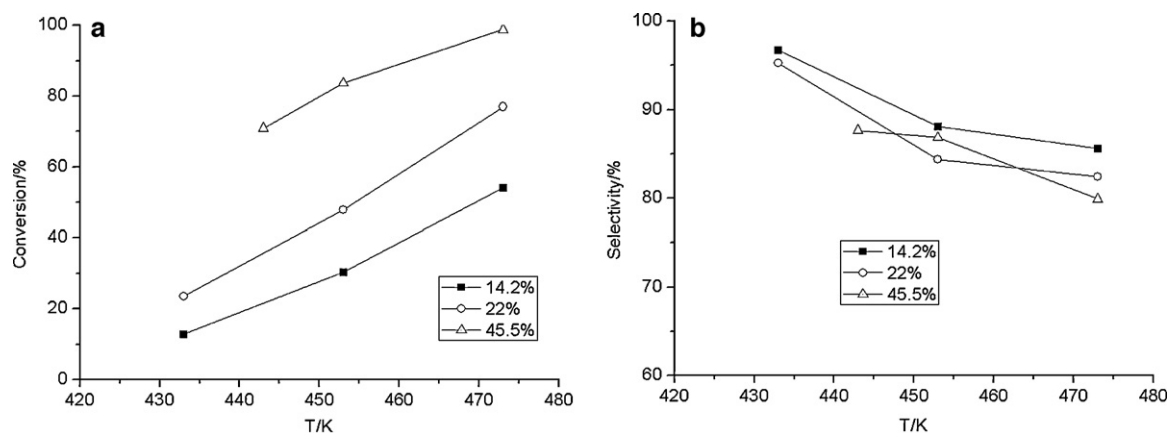| Chemical shift (ppm)	Multiplicity	Protons designation
0.98	Doublet	**CH$_3$**CH(OH)CH$_2$OH
1.05	Doublet	(**CH$_3$**)$_2$CHOH
2.03	Singlet	**CH$_3$**C(O)CH$_2$OH
3.33	ABX pattern	CH$_3$CH(OH)**CH$_2$**OH
3.73	Multiplet	CH$_3$**CH**(OH)CH$_2$OH
3.86	Septet	(CH$_3$)$_2$**CH**OH
4.12	Singlet	CH$_3$C(O)**CH$_2$**OH

Fig. 2. Effect of temperature and copper loading on methyl lactate conversion (a) and selectivity to propylene glycol (b) at hydrogen flow velocity of $10 L h^{-1}$ and liquid methyl lactate supply velocity of $0.4 mL h^{-1}$, methyl lactate/H_2 = 1:107 (molar ratio).

It can be superficially surprising if it is supposed that the catalytic activity is determined only by the metallic copper specific surface area. At the same time, according to Van Der Grift [30], an increase in the Cu loading from 5 to 40 wt.% gave a rise in the specific surface area of the catalyst precursors from 210 to $520 m^2/g$. Thus along with increasing copper loading simultaneously the support surface area also increases, which might lead to additional activity in some alkyl lactate transformation steps involving catalyst acidic sites. Therefore, it can be concluded that silica surface with supported on it copper crystallites plays an evident role in the discussed above catalytic reactions and improves the alkyl lactate reaction rate by acidic sites participation (see reaction scheme). Therefore, the highest catalytic activity of 45.5 wt.% Cu/SiO₂ catalyst seems to be associated with both high Cu metal dispersion and high specific surface area of the catalyst. Further experiments were performed using the most active 45.5 wt.% Cu/SiO₂ catalyst.

3.3. Effect of process parameters

As it is discussed above, ester hydrogenolysis can be performed in a batch mode as well as in a fixed-bed reactor. The latter option provides a number of advantages such as possibility of an in situ catalyst pre-activation (or regeneration), no catalyst attrition, no necessity to separate the catalyst from product mixture and ability to realize hydrogenolysis under lower hydrogen pressure because

of easy access to the active metal surface (avoiding mass transfer via the liquid phase).

To estimate the optimal reaction conditions influence of temperature on lactate conversion and selectivity to propylene glycol was studied first. It was found that increase of temperature leads to an increase of methyl and butyl lactate conversion as overall reaction rate grows but selectivity to desired propylene glycol decreases due to increase of hydroxyacetone formation (Fig. 4). Maximum propylene glycol yield of 76% obtained during methyl lactate hydrogenolysis was achieved at methyl lactate conversion of 98% and selectivity of 78% at 473 K (Fig. 4).

Effect of weight hourly space velocity (WHSV) on the reaction composition was studied in neat methyl lactate hydrogenolysis at temperatures 443, 473 and 493 K. For these catalytic runs the WHSV is calculated as grams of alkyl lactate fed to the reactor per one gram of catalyst per hour. It was found, that concentration of methyl lactate decreases and concentrations of main products increase with decreasing WHSV, related conversion dependence is illustrated in Fig. 5. It is important to note that propylene glycol and hydroxyacetone selectivities do not depend on WHSV i.e. on methyl lactate conversion (Fig. 6). Further discussion about reaction paths will be presented in Section 3.6. The most plausible explanation of this experimental fact is that hydroxyacetone is formed as a result of propylene glycol dehydrogenation even in the excess of hydrogen
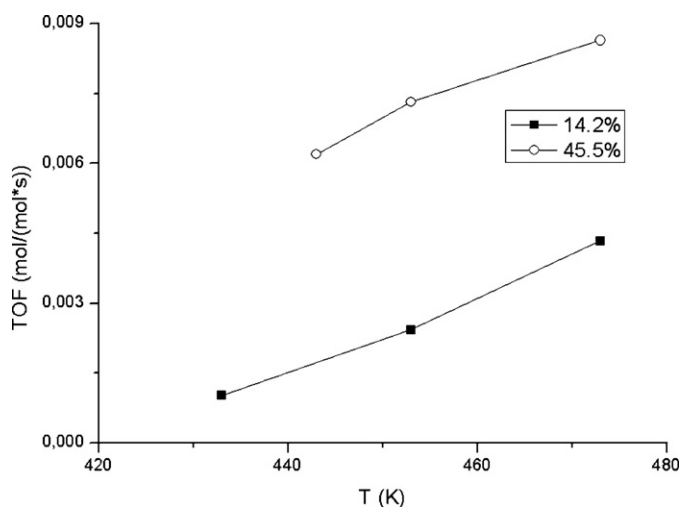

Fig. 3. Methyl lactate hydrogenolysis TOF dependence from temperature over 14.2 wt.% and 45.5 wt.% Cu/SiO₂ catalysts.
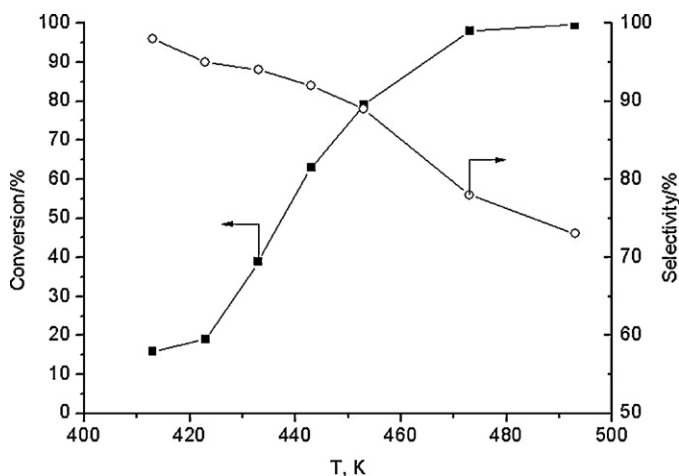

Fig. 4. Effect of temperature on methyl lactate conversion (■) and selectivity to propylene glycol (○) over 45.5% Cu/SiO₂, liquid supply velocity $0.2 mL h^{-1}$, methyl lactate/H_2 = 1:214 (molar ratio). Arrows show assignment of curves to the corresponding ordinate axes.
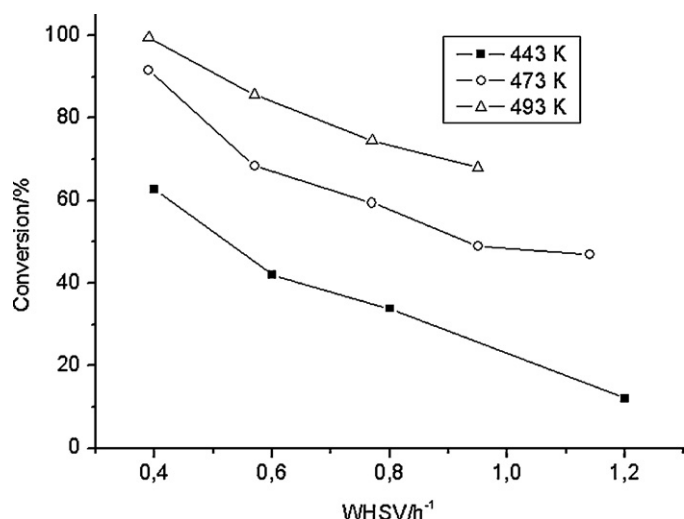
Fig. 5. Dependence of methyl lactate conversion on weight hourly space velocity (WHSV) at temperature 443, 473 and 493 K, hydrogen flow rate 10 L h^{-1}.
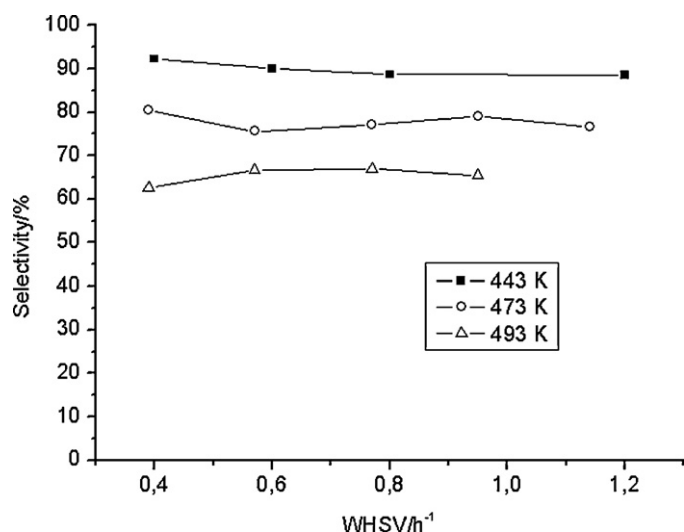

Fig. 6. Dependence of propylene glycol selectivity in methyl lactate hydrogenolysis as a function of WHSV at 443, 473 and 493 K, hydrogen flow rate 10 L h^{-1}.

and the rate of this reaction is higher, than rate of propylene glycol formation.

3.4. Effect of solvent

In order to reveal the role of solvent during hydrogenolysis, neat methyl lactate was dissolved in water and in methanol. Resulting solutions with methyl lactate concentration of 17 wt.% underwent hydrogenolysis at the optimal conditions (Table 3). In the presence of water the selectivity to propylene glycol decreased because of intensive side hydrolysis with the subsequent formation of lactic and propanoic acid. In the presence of methanol selectivity

Table 3
Effect of solvent on the formation of products in methyl lactate hydrogenation over Cu/SiO$_2$ catalyst at 473 K, WHSV = 0,18 h^{-1}, hydrogen flow rate 10 L h^{-1}.

Solvent	Hydroxy-acetone	Propanoic acid	Propylene glycol	Other by-products
Water	18.8	8.4	59.7	6.3
Methanol	6.4	1.2	74.7	16.6
None	21.2	–	73.9	4.8

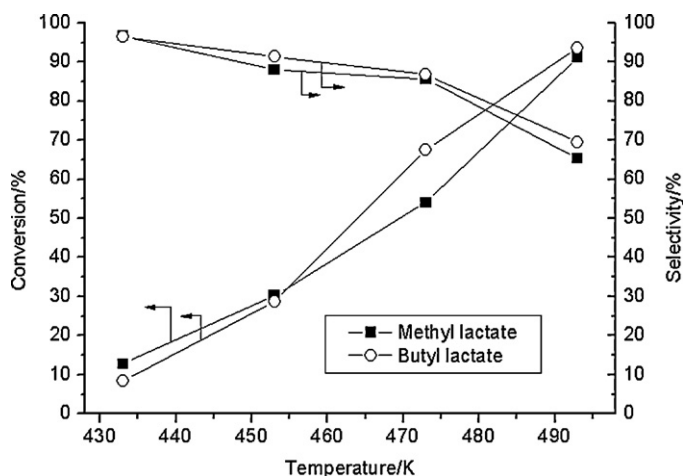**Fig. 7.** Conversion of methyl and butyl lactate and propylene glycol selectivity as a function of temperature. WHSV (methyl lactate) = 0.8 h^{-1} and WHSV (butyl lactate) = 1.2 h^{-1} respectively, hydrogen flow rate 10 L h^{-1}, alkyl lactate/H$_2$ = 1:107 (molar ratio). Arrows show assignment of curves to the corresponding ordinate axes.

was slightly increased, but methyl 2-methoxypropionate and methanol conversion products were detected in the reaction mixture. Methanol dehydrogenation to methyl formate over copper-containing catalysts [31,32] as well as methanol dehydration to dimethyl ester over solid-acid catalysts is well known [33,34]. The reactive ability of methanol leads to product contamination and irretrievable loss of methanol instead of being used in lactic acid esterification repeatedly. Although methanol is attractive being inexpensive and easily available in industry we are prone to avoid using methanol, because of its high reactivity in the presence of copper silica catalyst.

Eventually, in the presence of solvent hydrogenolysis of methyl lactate becomes less selective and more energy-consuming due to additional heating and vaporization of solvent compared with that for neat methyl lactate. Thus hydrogenolysis of neat alkyl lactate seems to be more selective and preferable.

3.5. Effect of alkyl substitute

For a comparative study of alkyl substitute effect neat butyl lactate and methyl lactate were hydrogenated under the same conditions. As shown in Fig. 7, conversion of methyl and butyl lactate increases concurrently when temperature increases. Temperature dependence of selectivity to propylene glycol, which is formed as a product of methyl or butyl lactate hydrogenolysis, seems to be also very similar giving nevertheless different by-product alcohols. Similar behavior of methyl and butyl lactates provides motivation to consider other aspects of alkyl fragment selection.

As it was shown above for methanol used as a solvent, methanol stoichiometrically released during hydrogenolysis of neat methyl lactate can react over Cu/SiO$_2$ catalyst via by-side dehydrogenation and dehydration to form methyl formate and dimethyl ester which results in additional methanol consumption not related with the main process. In the case of butyl lactate hydrogenolysis, contrary to that for methyl lactate, hydroxyacetone is the only by-product that can be easily separated from the targeted propylene glycol. At the same time no butanol losses were observed at the explored conditions and butanol released during hydrogenolysis can be quantitatively recycled back to preceding esterification step. In addition butanol is a promising esterification agent due to simplicity of butyl lactate synthesis via azeotropic distillation method [35]. To increase the yield of the resultant ester, water can
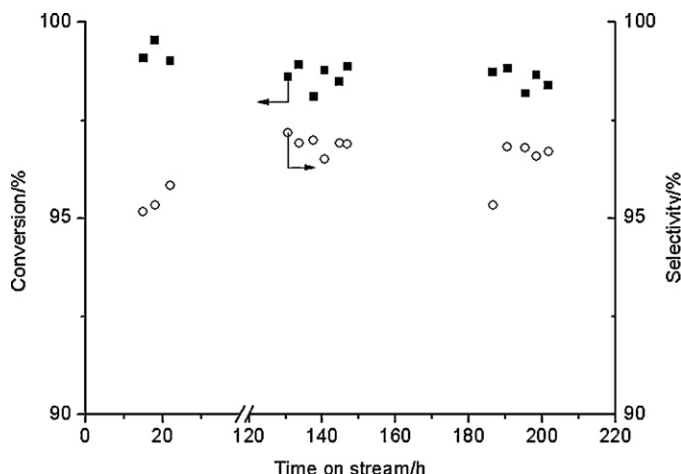
Fig. 8. Stability of 45.5 wt.% Cu/SiO$_2$ catalyst during butyl lactate hydrogenolysis. WHSV = 0.2 h^{-1}, hydrogen supply velocity of 10 L h^{-1}, 453 K. Arrows show assignment to the corresponding ordinate axes.

Fig. 9. Effect of residence time on products ratio during butyl lactate hydrogenolysis at different temperature.

be removed completely with excess of butanol rather than with methanol during ester synthesis.

Thus, butyl substitute is more attractive in lactate hydrogenolysis leading to propylene glycol selectivity of 96% at full conversion of initial substrate at 453 K (see Fig. 8). It can be suggested to utilize higher alcohols for lactic acid esterification before hydrogenolysis.

3.6. Hydrogenolysis reaction pathways

As it has been previously demonstrated, acidic sites on the surface of a catalyst are necessary for lactic acid hydrogenation, since according to various published data including our own catalytic tests (not shown here) the Raney copper is not capable to catalyze such reaction, while all copper-containing catalysts having Brønsted acidic sites are known to be able to activate lactic acid transformation [24,25]. Hemiacetals have been considered as key intermediates in hydrogenolysis of alkyl formates and fatty acid esters on copper–chromium catalysts [32]. They were previously observed in hydrogenolysis of ethyl trifluoroacetate, butyl heptafluorobutyrate and other perfluorinated esters [17]. From the mechanistic view point it is possible, that OH-groups on the surface of SiO$_2$ can promote hydrogenation step by protonation of carbonyl oxygen followed by hydrogen addition to form an intermediate hemiacetal [17]. Therefore, participation of surface protons in alkyl lactate transformation should be considered.

Since butyl lactate hydrogenolysis was found to be less complicated in terms of secondary transformations of primary formed reaction products, it was selected to elucidate lactate hydrogenolysis pathways. At the same time formation of hydroxyacetone can be considered as a side reaction of propylene glycol dehydrogenation over metallic copper particles. However, it was found that the ratio of products is changed depending on temperature but is independent on residence time (Fig. 9). According to the Arrhenius dependence apparent activation energies and pre-exponential factors were found to be respectively 89 kJ/mol and 1.4×10^8 s^{-1} for propylene glycol formation, and 117 kJ/mol and 1.5×10^{12} s^{-1} for hydroxyacetone formation reactions. Thus one can suggest that the equilibrium between propylene glycol and hydroxyacetone (1) is achieved. Using all data obtained from experiments on butyl lactate hydrogenolysis, propylene glycol dehydrogenation as well as hydroxyacetone hydrogenation estimated equilibrium constant of
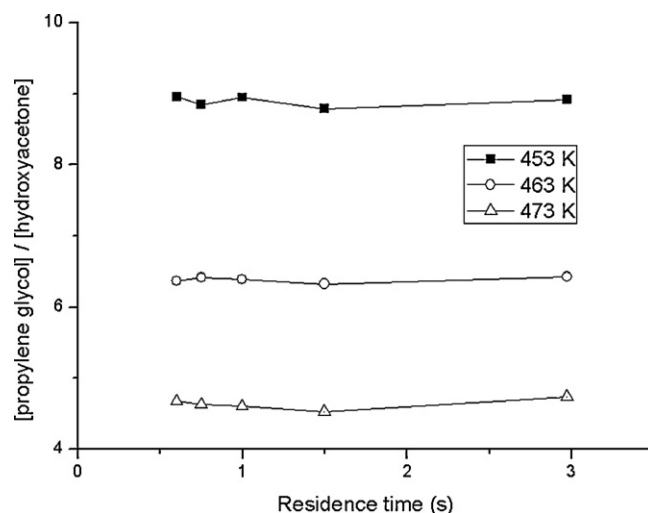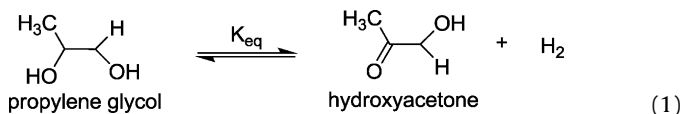
reaction (1) can be expressed as $\ln K_{eq} = 9.8 - 5.5 \times 10^3 \times T^{-1}$ where T is reaction temperature in K (Fig. 10b).

$$(1)$$

To confirm this hypothesis the reaction was commenced from the products – propylene glycol and hydroxyacetone. Dehydrogenation of neat propylene glycol as well as hydrogenation of neat hydroxyacetone was performed in hydrogen atmosphere (1 bar) at the same temperature (443, 473 and 493 K) as butyl lactate hydrogenolysis. As demonstrated in Fig. 10b, hydroxyacetone formation was observed from propylene glycol even in an excess of hydrogen, moreover propylene glycol was formed from hydroxyacetone. The ratio between propylene glycol and hydroxyacetone both in the forward (propylene glycol dehydrogenation) and in the backward reactions (hydroxyacetone hydrogenation) was inversely changed with reaction temperature. It means that hydrogenolysis mechanism apparently involves the equilibrium
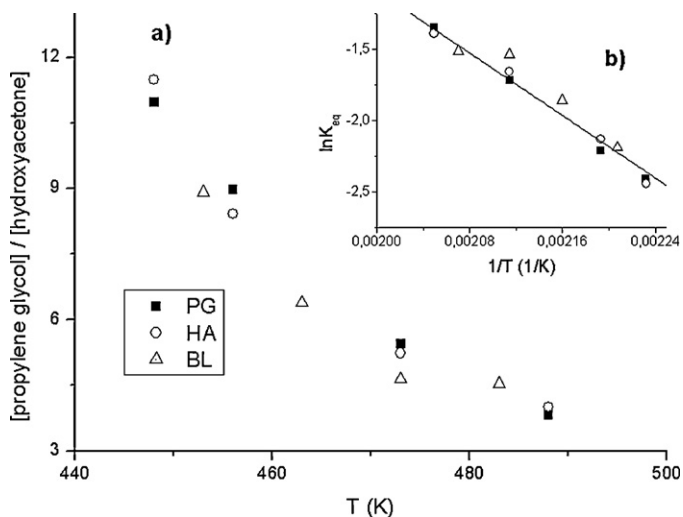

Fig. 10. Ratio of propylene glycol to hydroxyacetone vs. temperature (a) and temperature dependence of equilibrium constant K_{eq} (b) in propylene glycol dehydrogenation (PG), hydroxyacetone hydrogenation (HA) and butyl lactate hydrogenolysis (BL) over 45.5% Cu/SiO$_2$, substrate/H$_2$ = 1:70 (molar ratio).
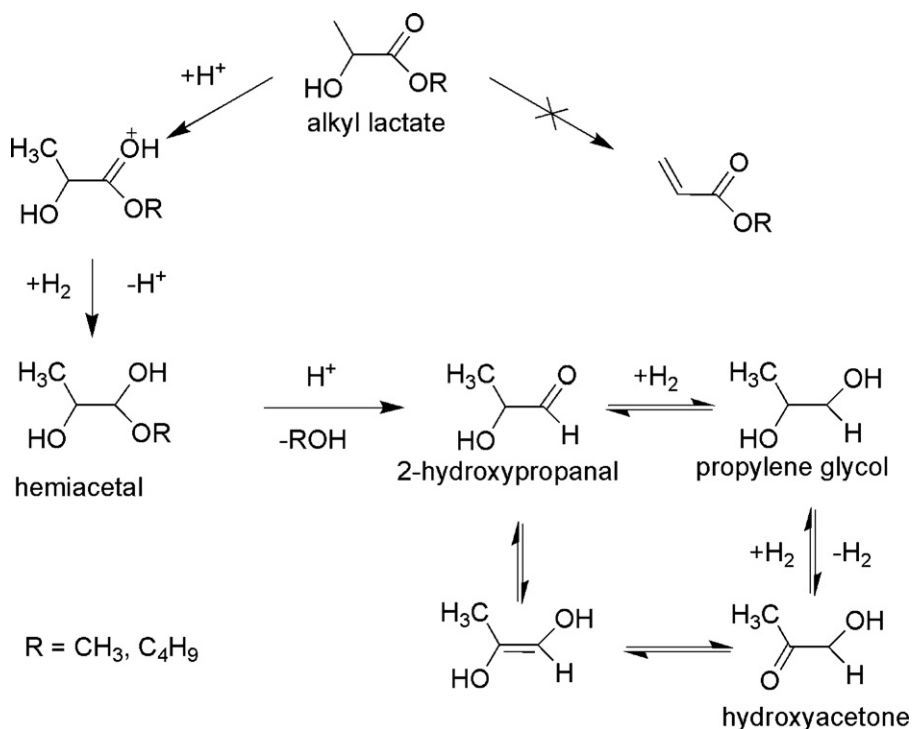
Fig. 11. Tentative scheme of alkyl lactate transformation over Cu/SiO$_2$ catalyst.

between propylene glycol and hydroxyacetone. This equilibrium seems to be controlled by hydrogen partial pressure and can be shifted to propylene glycol by the smallest increase of hydrogen pressure leading to selectivity of 100%. Note that the results obtained in this study are quite similar to that for fatty ester hydrogenolysis over copper catalysts where fast equilibrium was observed between the desired alcohol and the corresponding carbonyl compounds [12].The impact of internal diffusion was determined through evaluation of catalyst effectiveness factor for spherical catalyst particles with mean radius $R = 1.75 \times 10^{-4}$ m (fraction 250–500 μm) via estimation of the Thiele modulus. Calculation of the effectiveness factor for butyl lactate hydrogenolysis under reaction conditions gave a value 0.98, which is close to unity, indicating that alkyl lactate diffusion inside the catalyst pores does not affect the reaction rate notably.

A negligible impact of external diffusion can be shown taking into account that the lactates hydrogenolysis rate increases substantially with temperature and apparent activation energy calculated from the experimental data is 89 kJ/mol for propylene glycol formation and 117 kJ/mol for hydroxyacetone formation reactions. In case of external mass transfer limitations the enhancement of reaction rate with the temperature rise is insignificant and the apparent activation energy is close to 3–10 kJ/mol [36]. Consequently, this fact suggests that the mass transfer of vapor reaction mixture components to the catalyst surface occurs rapidly and does not limit the overall process.

Based on the kinetic data and the identification of intermediates by GC/MS and ^{1}H NMR a lactate transformation network over reduced silica-supported copper may be proposed (Fig. 11). This scheme seems to be similar to that for methyl formate hydrogenolysis over Cu/SiO$_2$ catalyst [25]. The main reaction path includes the adsorption of lactate on metallic copper with the acid-promoted protonation of the C—O bond of the carboxylic group followed by the hydrogenation of the C=O bond to form hemiacetal, which in parallel is converted into propylene glycol and hydroxyacetone providing thermodynamic equilibrium between them. The side path where alkyl lactate converted to alkyl acrylate followed by

polymerization blocked the active catalyst sites is completely suppressed. Thus, it is clear that active catalytic sites remain available for reactants and therefore the catalyst is stable on time-on-stream for a long period of time, as it is demonstrated in Fig. 8.

4. Conclusions

Silica-supported copper catalysts with different copper loading were tested in vapor-phase hydrogenolysis of methyl lactate at atmospheric hydrogen pressure. Hydrogenolysis conditions were optimized and the most active catalyst with copper loading 45.5 wt.% afforded 98% methyl lactate conversion and selectivity to propylene glycol of 78% at 473 K. The main by-product was hydroxyacetone. In the presence of water and methanol side reactions of hydrolysis and dehydration occur leading to selectivity drop, therefore the use of solvent should be avoided.

Effect of substituent in alkyl lactate on conversion and selectivity to propylene glycol was studied. Substrate conversion and selectivity to the main products were very similar during hydrogenolysis of neat methyl and butyl lactates. Utilization of butyl lactate is preferred due to resistance of released butanol to side transformations compared to methanol providing propylene glycol selectivity of 96% at nearly full butyl lactate conversion of 99% under atmospheric hydrogen pressure at 453 K.

The effect of space velocity was studied. Selectivity to propylene glycol and hydroxyacetone was found to be independent on alkyl lactate conversion at isothermal conditions. It was proposed, that propylene glycol and hydroxyacetone are thermodynamically equilibrated and this equilibrium is controlled by hydrogen partial pressure.

Based on the kinetic data and identification of intermediates by GC/MS and ^{1}H NMR an alkyl lactate hydrogenolysis routes over reduced silica-supported copper were proposed. The main reaction path involves consecutive lactate carbonyl moiety protonation and hydrogenation into hemiacetal followed by formation of thermodynamically equilibrated mixture of propylene glycol and hydroxyacetone with overwhelming majority of propylene glycol

whereas irreversible alkyl acrylate formation is completely suppressed.

Note that the developed process corresponds to the main principles of green chemistry since it occurs in the presence of catalysts with high selectivity, does not demand any solvent and minimizes possible wastes, utilizes and generates substances that possess no toxicity to human health and the environment and minimizes energy requirements operating under ambient hydrogen pressure. Furthermore, taking into account that commercial production of neat lactic acid is based on alkyl lactate ester distillation [37] it can be suggested that the obtained results make this catalytic way of propylene glycol synthesis from alkyl lactate more promising compared to the one from lactic acid if there are economic incentives for the market to utilize renewable resources instead of petroleum for propylene glycol synthesis.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcatb.2012.03.003.

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